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(54) Title: CO-PROCESSED YELLOW PIGMENTS

(57) Abstract: One aspect of the invention relates to a yellow pigment composition containing at least one yellow nickel titanate and at least one yellow organic pigment containing a benzimidazolone moiety. Another aspect of the invention relates to a method of making a yellow pigment composition involving the steps of combining at least one yellow nickel titanate and at least one yellow benzimidazolone pigment to form a mixture; and mixing the mixture to form a homogenous mixture of the yellow pigment composition.

## CO-PROCESSED YELLOW PIGMENTS

Field of the Invention

The present invention generally relates to yellow pigment compositions. In particular, the present invention relates to yellow pigment compositions containing co-processed organic pigments and inorganic pigments.

Background of the Invention

Many conventional organic pigment blends, when subjected to a hot melt heat test (temperatures of 200°C to 230°C for a period of four hours), 10 tend to decompose and discolor. Specifically, monoazo yellow pigments tend to undesirably bloom and discolor at high temperatures, so their use is disfavored. Disazo (diarylide) yellow pigments are much stronger tintorially and show a much lower tendency to bloom and discolor at high temperatures. However, R. Az et al reports in *Dyes and Pigments*, 15, 1 (1991), that 15 diarylide yellows are degraded to potentially carcinogenic by-products (e.g., 3,3'-dichlorobenzidine) in plastics processed above 200°C, a temperature lower than that used in processing most plastics (many plastics are processed at temperatures from 250°C to 330°C).

Most yellow pigments have one or two desirable properties in addition 20 to several undesirable properties. For example, some yellow pigments are strong, but have poor weathering characteristics, poor heat resistance, undesirable tints and/or shades, and/or costly starting materials. Other yellow pigments have good weathering characteristics, but have poor heat 25 resistance, are weak, have undesirable tints and/or shades, and/or costly starting materials.

Given these circumstances, when employing yellow pigments, one must accept a compromise on at least one desirable property. There is thus

an unmet need in the art for yellow pigments having many desirable properties.

#### Summary of the Invention

The present invention provides yellow pigment compositions containing 5 co-processed organic pigments and inorganic pigments. The co-processed pigments have improved color properties as well as improved heat stability and weathering. In particular, the improved color properties of the co-processed pigments include desirable chroma, high color strength, and excellent lightfastness. The co-processed yellow pigments of the present 10 invention are inexpensive to produce compared to other commercially available yellow pigment compositions. Moreover, in some embodiments, the co-processed yellow pigments of the present invention do not contain chlorine, and thus do not breakdown into potentially harmful chlorine containing components.

15 One aspect of the invention relates to yellow pigment composition containing at least one yellow nickel titanate and at least one yellow organic pigment containing a benzimidazolone moiety.

20 Another aspect of the invention relates to a yellow pigment composition containing from about 5% to about 80% by weight of at least one yellow nickel titanate and from about 20% to about 95% by weight of at least one yellow benzimidazolone pigment.

25 Yet another aspect of the invention relates to a method of making a yellow pigment composition involving the steps of combining at least one yellow nickel titanate and at least one yellow benzimidazolone pigment to form a mixture; and mixing the mixture to form a homogenous mixture of the yellow pigment composition.

#### Detailed Description of the Invention

The present invention provides yellow pigment compositions containing 30 at least co-processed yellow organic pigments and yellow inorganic pigments.

The yellow pigment compositions may optionally contain additional pigments and/or additives. The yellow organic pigment and yellow inorganic pigment are co-processed in that an intimate mixture is formed. The yellow pigment compositions of the present invention contain at least a yellow nickel titanate 5 as an inorganic pigment and a yellow benzimidazolone as an organic pigment.

While not wishing to be bound by any theory, it is believed that the formation of a stable composition with desirable properties is facilitated by surface to surface interactions between the oxide inorganic pigment and the 10 benzimidazolone moiety of the organic pigment.

Yellow nickel titanate pigment is an inorganic pigment derived from a mixture of nickel oxide and titanium oxide and optionally antimony oxide. Nickel titanate has the general formula  $\text{NiTiO}_3$ . In one embodiment, the 15 yellow nickel titanate pigment is Pigment Yellow 53. Pigment Yellow 53 may be prepared by calcining a mixture of antimony oxide, nickel oxide and titanium oxide. Pigment Yellow 53 is commercially available from numerous sources, including Cerdec under the tradename of Irgacolor Yellow 10401. The yellow nickel titanate pigments are typically available in powder form.

Yellow nickel titanate pigments, including methods of their preparation, 20 are found in the Pigment Handbook, Vol. 1, pp. 419-427 (1973), which is incorporated herein by reference. Generally, yellow nickel titanate pigments can be made by either precipitation or by calcination. The calcination process is characterized by a mixing of the raw materials required for the particular 25 pigment (mixing can be conducted by dry blending or by wet milling, for example). The mixture is then calcined at a high temperature, such as at about 980°C. After firing, the pigment is wet milled in a ball mill. The milled product is transferred to a filter press where it is washed and then dewatered to produce a filtercake. The filtercake is then dried and passed through a micropulverizer to produce a fine powder. The final step in the manufacturing 30 process is to blend various batches to ensure that the finished product meets the quality control specifications for the pigment. Yellow nickel titanates can

also be prepared by a precipitation process using a nickel salt with titanium dioxide, which is hydrated, and antimony oxide. The mixture is dried and calcined in the same manner as for the dry blended material.

In one embodiment, the yellow pigment compositions of the present invention contain from about 5% to about 80% by weight of at least one yellow nickel titanate inorganic pigment. In another embodiment, the yellow pigment compositions contain from about 10% to about 70% by weight of at least one yellow nickel titanate inorganic pigment. In yet another embodiment, the yellow pigment compositions contain from about 15% to 10 about 60% by weight of at least one yellow nickel titanate inorganic pigment.

Yellow benzimidazolones are organic pigments containing a benzimidazolone moiety in its chemical structure. Benzimidazolones are azo organic pigments generally derived from an aromatic amine and a benzimidazolone coupler, wherein the aromatic amine is initially diazotized 15 and then coupled to the benzimidazolone coupler. The coupling mixture may be heated, such as at temperatures over 100°C. The yellow benzimidazolones may be monoazo organic pigments or disazo organic pigments.

In one embodiment, the yellow pigment compositions of the present invention contain from about 20% to about 95% by weight of at least one yellow benzimidazolone organic pigment. In another embodiment, the yellow pigment compositions contain from about 30% to about 90% by weight of at least one yellow benzimidazolone organic pigment. In yet another embodiment, the yellow pigment compositions contain from about 40% to 25 about 85% by weight of at least one yellow benzimidazolone organic pigment.

Benzimidazolones organic pigment compositions and methods of preparing such are generally described in U.S. Patents 4,080,321; 4,392,999; 4,555,568; 4,664,714; 5,352,281; and 5,756,757; which are hereby incorporated by reference in this regard.

30 Benzimidazolones organic pigment compositions are commercially available from a number of sources. The yellow benzimidazolone pigments

are typically available in powder form. Examples of benzimidazolone organic pigments include Pigment Yellow 120, Pigment Yellow 151, Pigment Yellow 154, Pigment Yellow 156, and Pigment Yellow 175. The chemical formulae of some of these pigments are as follows:

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Pigment Yellow 151

Pigment Yellow 154

### Pigment Yellow 175

The yellow pigment compositions may optionally contain additional organic and/or inorganic pigments and/or additives. In one embodiment, the yellow pigment compositions contain from about 0.01% to about 20% by weight of additional organic and/or inorganic pigments and/or additives. In another embodiment, the yellow pigment compositions contain from about 0.1% to about 15% by weight of additional organic and/or inorganic pigments and/or additives. In another embodiment, the yellow pigment compositions contain from about 0.5% to about 10% by weight of additional organic and/or inorganic pigments and/or additives.

Examples of optional inorganic pigments include titanium dioxide, bismuth vanadate, lead chromate, cadmium zinc sulfide, cadmium barium sulfide, cadmium sulfide, potassium cobaltnitrite, lead antimoniate, nickel chromium compounds, and iron oxide. Specific examples of optional inorganic pigments include Pigment Yellow 34, Pigment Yellow 35, Pigment Yellow 37, Pigment Yellow 40, Pigment Yellow 41, Pigment Yellow 42, and Pigment Yellow 184.

Examples of optional organic pigments include isoindolinone pigments, arylide pigments, diarylide pigments, anthrapyrimidine pigments, quinophthalone pigments, nickel azomethine pigments, and pyrazolone

5       pigments. Specific examples of optional organic pigments include Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 55, Pigment Yellow 10, Pigment Yellow 11, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 16, Pigment Yellow 17, Pigment Yellow 61, Pigment Yellow 62, Pigment Yellow 65, Pigment Yellow 74, Pigment Yellow 81, Pigment Yellow 83, Pigment Yellow 93, Pigment Yellow 94, Pigment Yellow 95, Pigment Yellow 97, Pigment Yellow 98, Pigment Yellow 108, Pigment Yellow 110, Pigment Yellow 138, Pigment Yellow 139, Pigment Yellow 150, Pigment Yellow 152, Pigment Yellow 183, and Pigment Yellow 191.

10 Additives that may be optionally incorporated into the yellow pigment blends include glass beads, fillers, plasticizers, extenders, silicon dioxide, clays such as kaolin, calcium carbonate, diatomaceous earth, surfactants, dispersants, and solvents (generally for paint formulations).

15 In one embodiment, neither the yellow organic pigment nor the yellow inorganic pigment contain an atom of chlorine. Potential degradation products do not consequently pose safety and/or environmental problems. In another embodiment, the optional additional organic and/or inorganic pigments do not contain an atom of chlorine.

20 The yellow pigment compositions of the present invention are made by combining and mixing the yellow organic pigment and yellow inorganic pigment to form a homogenous mixture in any suitable manner. In other words, the yellow pigment compositions of the present invention are co-processed.

25 For example, in one embodiment, the yellow pigment compositions of the present invention are made by combining the yellow organic pigment and yellow inorganic pigment (and optionally one or more additives), dry blending the mixture, and then grinding or dry milling the mixture. Alternatively, the yellow pigment compositions of the present invention are made by combining the yellow organic pigment and yellow inorganic pigment (and optionally one or more additives), grinding the mixture, and then dry blending the mixture. In 30 both of these instances, one or more additives can be optionally added before

or after forming the mixture, blending the mixture, or grinding the mixture.

In another embodiment, the yellow pigment compositions of the present invention are made by combining the yellow organic pigment and yellow inorganic pigment (and optionally one or more additives) with a liquid such as water to form a slurry, optionally mixing the slurry (such as wet milling the slurry), spray drying the slurry, and then optionally grinding the spray dried mixture. One or more additives can be optionally added before or after forming the slurry, mixing the slurry, spray drying the slurry, or grinding the spray dried mixture.

In yet another embodiment, the yellow pigment compositions of the present invention are made by combining the yellow organic pigment and yellow inorganic pigment (and optionally one or more additives) with a liquid such as water to form a slurry, optionally mixing the slurry (such as wet milling the slurry), spin flash drying the slurry, and then optionally grinding the spin flash dried mixture. One or more additives can be optionally added before or after forming the slurry, mixing the slurry, spin flash drying the slurry, or grinding the spin flash dried mixture.

In still yet another embodiment, the yellow pigment compositions of the present invention are made by simply combining the yellow organic pigment and yellow inorganic pigment (and optionally one or more additives) and mixing the components in one or more of blender, such as a cone blender, mixer (wet or dry mixer), grinder, pulverizer, and the like.

The pigment compositions of the present invention provide yellow pigments having improved color strength, resistance to polar solvents, light fastness and/or heat stability and are useful as coloring agents in plastics, coatings and inks. In a preferred embodiment, the pigment compositions of the present invention provide yellow pigments having both improved color strength and improved heat stability.

In one embodiment, the pigment compositions of the present invention retain heat stability (do not substantially degrade or thermally breakdown) at temperatures up to and above about 275°C. In another the pigment

compositions of the present invention retain heat stability at temperatures up to and above about 280°C. In yet another the pigment compositions of the present invention retain heat stability at temperatures up to and above about 285°C. In still yet another the pigment compositions of the present invention 5 retain heat stability at temperatures up to and above about 290°C (for example, from about 275°C to about 295°C).

In other embodiments, therefore, the present invention relates to coating compositions including paint compositions, ink compositions and plastic compositions respectively comprising major amounts of a coating 10 vehicle such as a paint vehicle, ink vehicle or a plastic and minor amounts of the yellow pigment compositions. A major amount is at least 50% by weight. A minor amount is less than 50% by weight.

The coating, ink and plastic compositions in which the yellow pigment compositions are useful are well known to those of ordinary skill in the art. 15 Examples of inks include printing inks and lacquers, and plastics include thermoplastic and thermosetting materials, natural resins and synthetic resins, polystyrene and its mixed polymers, polyolefins, in particular polyethylene and polypropylene, polyacrylic compounds, polyvinyl compounds, for example polyvinyl chloride and polyvinyl acetate, polyesters 20 and rubber, and also filaments made of viscose and cellulose ethers and cellulose esters, such as ethylcellulose, nitrocellulose, cellulose acetate or cellulose butyrate, aminoplasts, in particular urea- and melamine-formaldehyde resins, alkyd resins, acrylic resins, phenoplasts, polycarbonates, polyamides, polyurethanes, casein, silicone and silicone 25 resins, polyesters, for example polyglycol terephthalates, and polyacrylonitrile. The yellow pigment compositions are also useful for pigment printing and for the pigmenting of paper in the mass.

Due to its excellent heat resistance, the pigment is in particular suitable 30 for the pigmenting of plastics in the mass, such as, for example, of polystyrene and its mixed polymers, polyolefins, in particular polyethylene and polypropylene and the corresponding mixed polymers, polyvinyl chloride and

polyesters in particular polyethylene glycol terephthalate and polybutylene terephthalate and the corresponding mixed condensation products based on polyesters, and mixtures and copolymers thereof.

5 Examples of coating compositions include paint compositions, adhesive compositions, and powder compositions. Thus, coating compositions include liquid based coating compositions and powder based coating compositions.

See, for example, with regard to ink: R.H. Leach, editor, The Printing Ink Manual, Fourth Edition, Van Nostrand Reinhold (International) Co. Ltd., 10 London (1988), particularly pages 282-591; with regard to coatings and paints: C.H. Hare, Protective Coatings, Technology Publishing Co., Pittsburgh (1994), particularly pages 63-288; and with regard to plastics: T.G. Webber, Coloring of Plastics, John Wiley & Sons, New York (1979), particularly pages 15 79-204. The foregoing references are hereby incorporated by reference for their teachings of coating, ink, and plastic compositions, formulations and vehicles in which the pigment compositions of the present invention may be used including amounts of colorants.

20 The following examples illustrate the present invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Centigrade, and pressure is at or near atmospheric pressure.

#### Example 1

25 A pigment composition is made by combining 20 g of Pigment Yellow 53 and 80 g of Pigment Yellow 120 and mixing in a blender.

#### Example 2

A pigment composition is made by combining 30 g of nickel titanate and 70 g of Pigment Yellow 151 and mixing in a blender.

#### Example 3

30 A pigment composition is made by combining 40 g of Pigment Yellow 53 and 60 g of Pigment Yellow 154 and mixing in a blender.

Claims

What is claimed is:

1. A yellow pigment composition comprising  
at least one yellow nickel titanate; and  
5 at least one yellow organic pigment containing a  
benzimidazolone moiety.
2. The yellow pigment composition according to claim 1, wherein  
the yellow pigment composition comprises from about 10% to about 70% by  
weight of yellow nickel titanate and from about 30% to about 90% by weight  
10 of the yellow organic pigment containing the benzimidazolone moiety.
3. The yellow pigment composition according to claim 1, wherein  
the yellow nickel titanate comprises Pigment Yellow 53.
4. The yellow pigment composition according to claim 1, wherein  
the yellow organic pigment containing the benzimidazolone moiety comprises  
15 at least one of Pigment Yellow 120, Pigment Yellow 151, Pigment Yellow 154,  
Pigment Yellow 156, and Pigment Yellow 175.
5. The yellow pigment composition according to claim 1, further  
comprising at least one of titanium dioxide, bismuth vanadate, lead chromate,  
cadmium zinc sulfide, cadmium barium sulfide, cadmium sulfide, potassium  
20 cobaltnitrite, lead antimoniate, nickel chromium compounds, and iron oxide.
6. The yellow pigment composition according to claim 1, further  
comprising at least one of an isoindolinone pigment, an arylide pigment, a  
diarylide pigment, an anthropyrimidine pigment, a quinophthalone pigment, a  
nickel azomethine pigment, and a pyrazolone pigment.
- 25 7. A yellow pigment composition comprising

from about 5% to about 80% by weight of at least one yellow nickel titanate; and

from about 20% to about 95% by weight of at least one yellow benzimidazolone pigment.

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8. The yellow pigment composition according to claim 7, wherein the yellow nickel titanate comprises Pigment Yellow 53 and the yellow benzimidazolone pigment comprises at least one of Pigment Yellow 120, Pigment Yellow 151, Pigment Yellow 154, Pigment Yellow 156, and Pigment 10 Yellow 175.

9. The yellow pigment composition according to claim 7, wherein the yellow pigment composition comprises from about 15% to about 60% by weight of at least one yellow nickel titanate and from about 40% to about 85% by weight of at least one yellow benzimidazolone pigment.

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10. The yellow pigment composition according to claim 9, wherein the yellow nickel titanate comprises Pigment Yellow 53 and the yellow benzimidazolone pigment comprises Pigment Yellow 151.

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11. The yellow pigment composition according to claim 7, further comprising at least one of glass beads, a filler, a plasticizer, an extender, silicon dioxide, a clay, calcium carbonate, diatomaceous earth, a surfactant, a dispersant, and a solvent.

12. The yellow pigment composition according to claim 7, wherein the yellow pigment composition has heat stability at temperatures up to and above about 275°C.

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13. The yellow pigment composition according to claim 7, wherein the yellow pigment composition has heat stability at temperatures up to and

above about 285°C.

14. A method of making a yellow pigment composition comprising combining at least one yellow nickel titanate and at least one yellow benzimidazolone pigment to form a mixture; and

5 mixing the mixture to form a homogenous mixture of the yellow pigment composition.

15. The method according to claim 14, wherein the yellow nickel titanate comprises Pigment Yellow 53 and the yellow benzimidazolone pigment comprises at least one of Pigment Yellow 120, Pigment Yellow 151, 10 Pigment Yellow 154, Pigment Yellow 156, and Pigment Yellow 175.

16. The method according to claim 14, wherein the mixture is a slurry formed by combining at least one yellow nickel titanate, at least one yellow benzimidazolone pigment, and water, further comprising drying the mixture to form the homogenous mixture of the yellow pigment composition.,

15 17. The method according to claim 16, wherein drying the mixture comprises spray drying the mixture.

18. The method according to claim 16, wherein drying the mixture comprises spin flash drying the mixture.

20 19. The method according to claim 14, further comprising grinding the mixture to form the homogenous mixture of the yellow pigment composition.

20. A coating composition comprising a coating vehicle and the yellow pigment composition according to claim 1.

21. A coating composition according to claim 20, wherein the coating vehicle is a paint.

22. A coating composition comprising a coating vehicle and the yellow pigment composition made by the method of claim 14.

5 23. An ink composition comprising an ink vehicle and the yellow pigment composition according to claim 1.

24. A plastic composition comprising a plastic vehicle and the yellow pigment composition according to claim 1.

10 25. The plastic composition according to claim 24, wherein the plastic vehicle comprises at least one of a polystyrene, a polyolefin, a polyacrylic compound, a polyvinyl compound, a polyester, a rubber, a cellulose ether, a cellulose ester, an aminoplast resin, an alkyd resin, an acrylic resin, a phenoplast resin, a polycarbonate, a polyamide, a polyurethane, casein, a silicone resin, a polyester, and a polyacrylonitrile.

15

26. A plastic composition comprising a plastic vehicle and the yellow pigment composition according to claim 7.

20 27. The plastic composition according to claim 26, wherein the plastic vehicle comprises at least one of a polystyrene, a polyolefin, a polyacrylic compound, a polyvinyl compound, a polyester, a rubber, a cellulose ether, a cellulose ester, an aminoplast resin, an alkyd resin, an acrylic resin, a phenoplast resin, a polycarbonate, a polyamide, a polyurethane, casein, a silicone resin, a polyester, and a polyacrylonitrile.

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28. A plastic composition comprising a plastic vehicle and the yellow pigment composition made by the method of claim 14.

29. The plastic composition according to claim 28, wherein the plastic vehicle comprises at least one of a polystyrene, a polyolefin, a polyacrylic compound, a polyvinyl compound, a polyester, a rubber, a cellulose ether, a cellulose ester, an aminoplast resin, an alkyd resin, an acrylic resin, a phenoplast resin, a polycarbonate, a polyamide, a polyurethane, casein, a silicone resin, a polyester, and a polyacrylonitrile.

## INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09B29/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category <sup>*</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 036 764 A (GOODING KIM DIANE ET AL) 14 March 2000 (2000-03-14) column 1, line 34 - line 39; claim 1 ----	1-29
Y	US 4 222 788 A (LIEDEK EGON ET AL) 16 September 1980 (1980-09-16) column 1, line 1 - line 13; claim 1 ----	1-29
Y	US 4 226 634 A (DIMROTH PETER ET AL) 7 October 1980 (1980-10-07) column 1, line 1 - line 15; claim 1 ----	1-29
Y	US 4 080 321 A (KUNSTMANN WALTER ET AL) 21 March 1978 (1978-03-21) cited in the application the whole document -----	1-29

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/US 01/42300

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6036764	A	14-03-2000	CA JP	2240307 A1 11029735 A	13-12-1998 02-02-1999
US 4222788	A	16-09-1980	AT AT BE CH DE DK FR GB JP NL SE SE	355692 B 51878 A 873684 A1 639410 A5 2855944 A1 28579 A ,B, 2415129 A1 2014596 A ,B 54112933 A 7900573 A ,B, 430511 B 7900550 A	10-03-1980 15-08-1979 16-05-1979 15-11-1983 30-08-1979 25-07-1979 17-08-1979 30-08-1979 04-09-1979 26-07-1979 21-11-1983 25-07-1979
US 4226634	A	07-10-1980	AT AT BE CH DE DK FR GB JP JP JP NL SE SE	355149 B 51778 A 873683 A1 639684 A5 2855943 A1 28479 A 2415128 A1 2017130 A ,B 1057084 C 54112934 A 55047061 B 7900572 A 430512 B 7900549 A	11-02-1980 15-07-1979 16-05-1979 30-11-1983 26-07-1979 25-07-1979 17-08-1979 03-10-1979 31-07-1981 04-09-1979 27-11-1980 26-07-1979 21-11-1983 25-07-1979
US 4080321	A	21-03-1978	DE AR AU BE CA CH DK FR GB IN IT JP JP JP NL AU	2338973 A1 203117 A1 7189174 A 818406 A1 1034117 A1 611641 A5 410074 A ,B, 2239495 A1 1473556 A 140885 A1 1017726 B 1224193 C 50071721 A 58053024 B 7410102 A 8183275 A	06-03-1975 14-08-1975 05-02-1976 03-02-1975 04-07-1978 15-06-1979 01-04-1975 28-02-1975 18-05-1977 01-01-1977 10-08-1977 15-08-1984 13-06-1975 26-11-1983 04-02-1975 09-12-1976